Implication of Atmospheric Wetness Levels on Corrosion at a Coating Defect during Accelerated Testing

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ASETS Defense
8/28/2012

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **28 AUG 2012**	2. REPORT TYPE	3. DATES COVERED **00-00-2012 to 00-00-2012**

4. TITLE AND SUBTITLE **Implication of Atmospheric Wetness Levels on Corrosion at a Coating Defect during Accelerated Testing**	5a. CONTRACT NUMBER 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER 5e. TASK NUMBER 5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Southwest Research Institute,6220 Culebra Rd,San Antonio,TX,78238-5166**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR’S ACRONYM(S) 11. SPONSOR/MONITOR’S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES
ASETSDefense 2012: Sustainable Surface Engineering for Aerospace and Defense Workshop, August 27-30, 2012, San Diego, CA. Sponsored by SERDP/ESTCP.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**19**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

Background

- SERDP program to develop improved accelerated corrosion test
- Many accelerated environmental tests exist
  - Developed by applying reasonable environmental conditions and ensuring resultant corrosion damage of a test system is realistic: **may or may not "excite" specific operational failure modes in other systems**
- Approach to new accelerated corrosion test
  - Thoughtful consideration of appropriate sample design
  - Make use of scientific understanding of corrosion mechanisms to develop exposure test cycle parameters

Outline

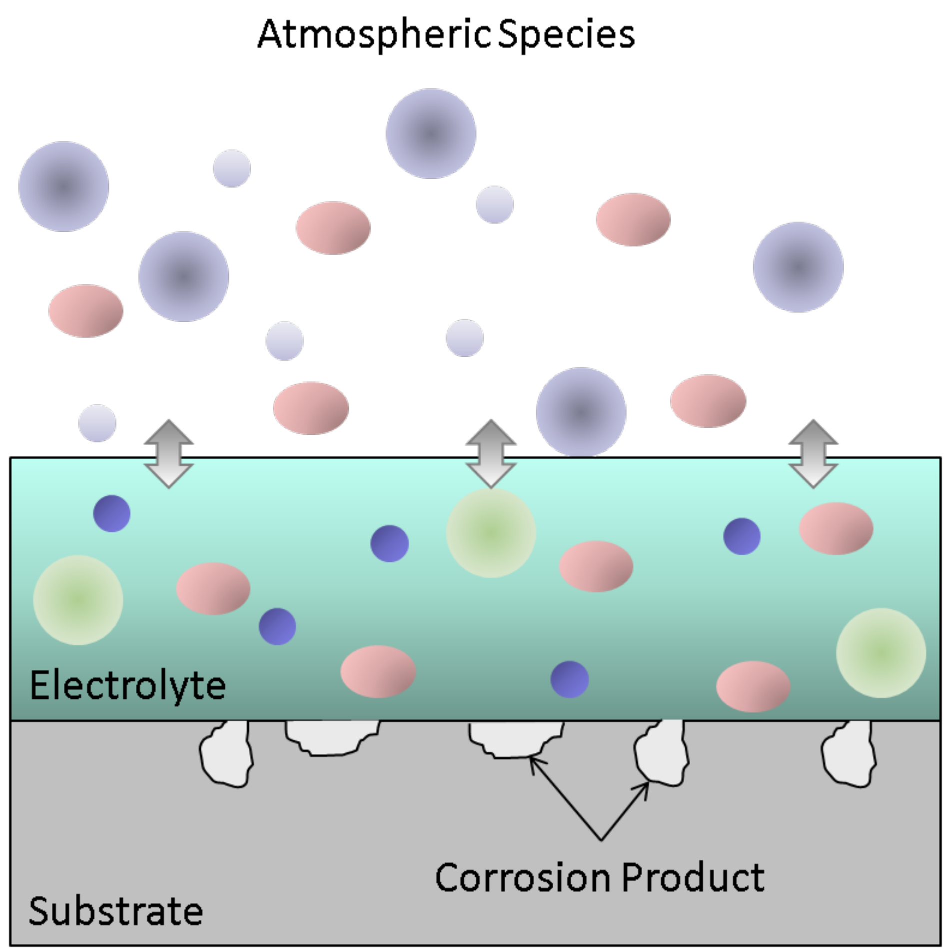
- Objectives
- Atmospheric corrosion
- Testing Approach
- Effect of RH on corrosion of steel
- Effect of inhibitor addition on coated steel
- Summary and future work

Technical Objective

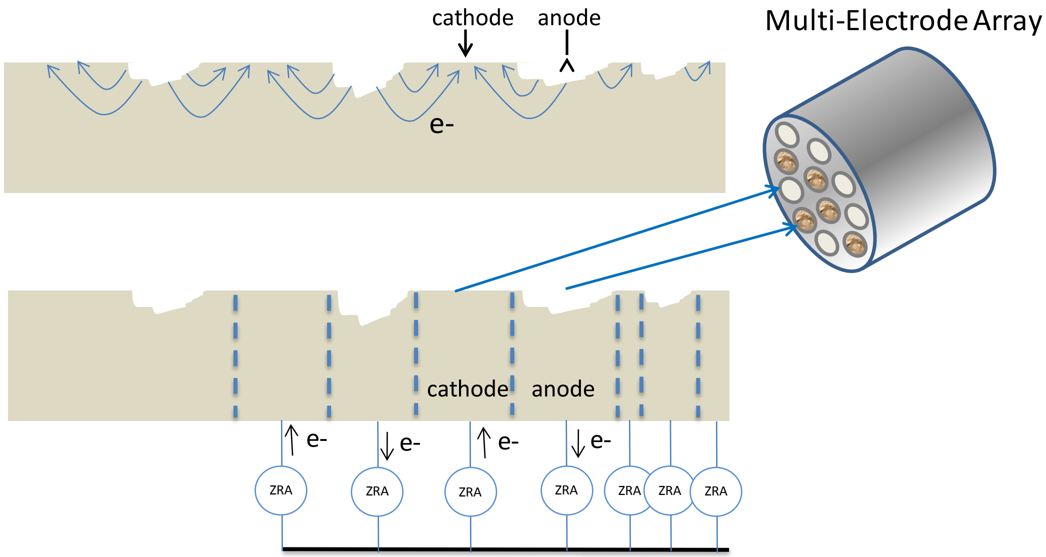
- **Objective**
  - Develop an understanding of how RH affect corrosion rate and perturbations in corrosion rate with inhibited coatings
- Why is understanding of RH effect important?
  - SAEJ2334 shows best correlations with field. Performed under wet bottom RH conditions (NOT FOG)
  - Cyclic conditions lead to different corrosion modes
  - SCC observed at salt deliquescence
  - Realistic conditions failure modes must be replicated in appropriate accelerated test methods

Atmospheric Corrosion

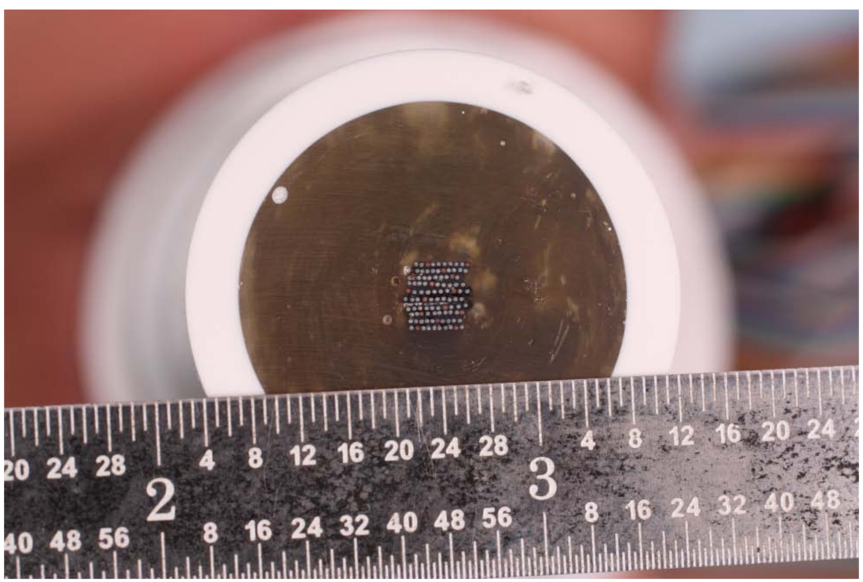
- Corrosion processes in the atmosphere are controlled by a thin film electrolyte layer on a metal substrate
- The electrolyte layer composition is controlled by
  - Atmospheric constituents (aerosols and gasses)
  - Relative Humidity (RH) and temperature
  - The presence of inhibitors in or galvanic interactions with coatings

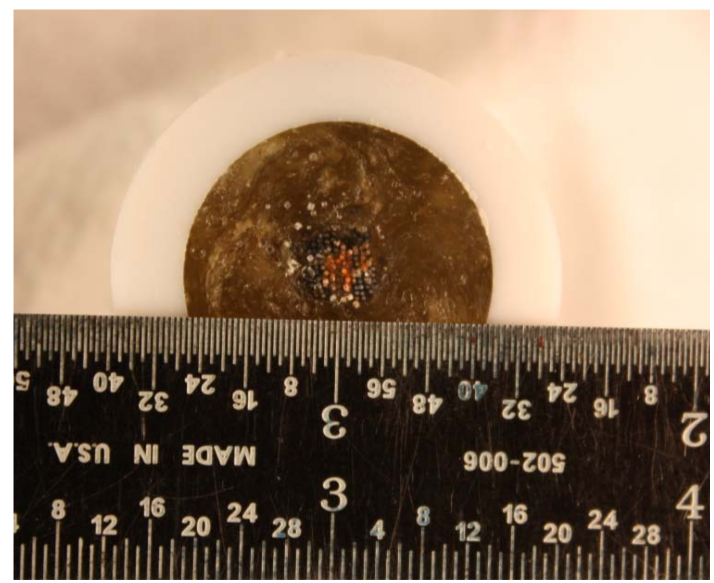


Experimental Approach



- Corrosion (anodic site) and reduction (cathodic site) occur at the same rate
- Electrons flow from anode to cathode
- Multiple isolated anodes or cathodes develop
- Measure current at each electrode gives corrosion rate at the corrosion potential



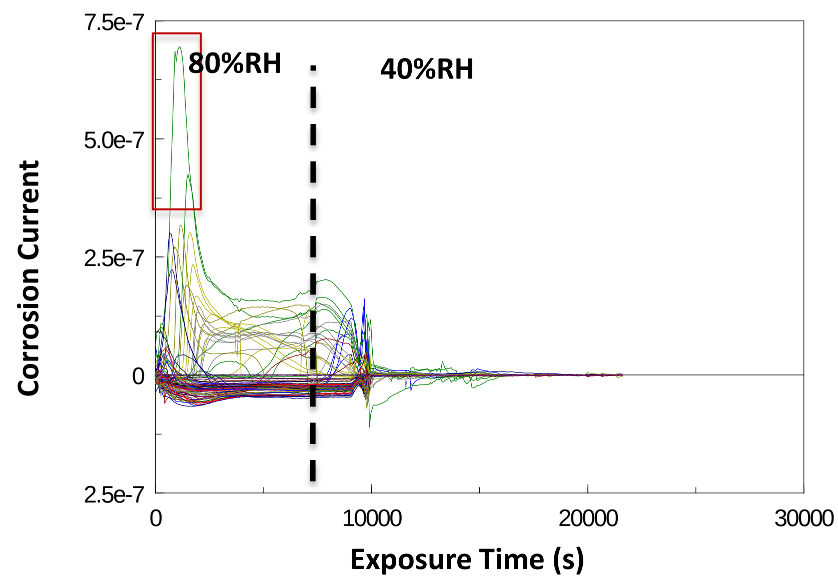


Experimental Procedure

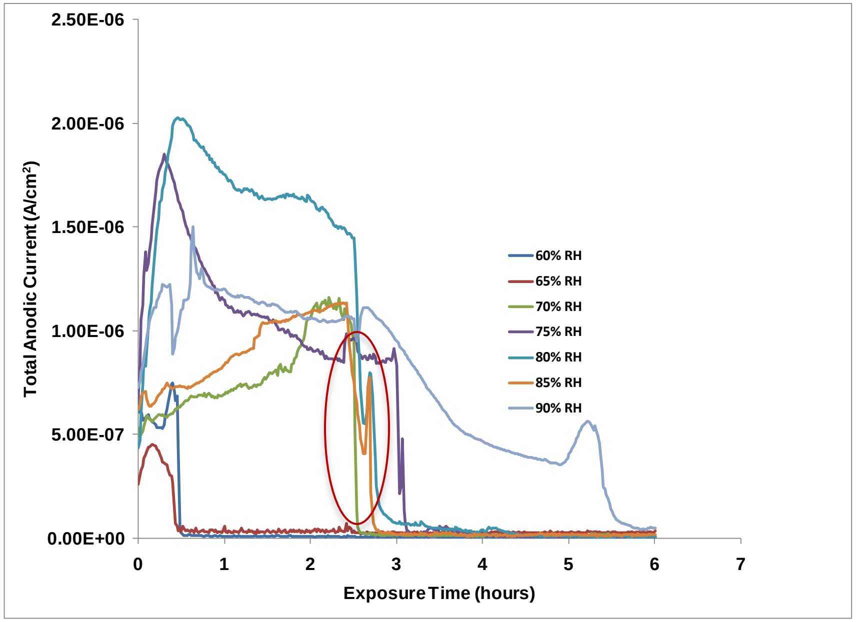
- 100 electrode (250 micron) multi-electrode probe fabricated using 1018 carbon steel
- ~10mg/cm^2 of NaCl placed over electrode elements (factor of 10 – 100 greater than outdoors)
- Atmospheric chamber used to control RH and temp
- Exposed under different RH conditions for 2.5 hour followed by reducing RH to 40%

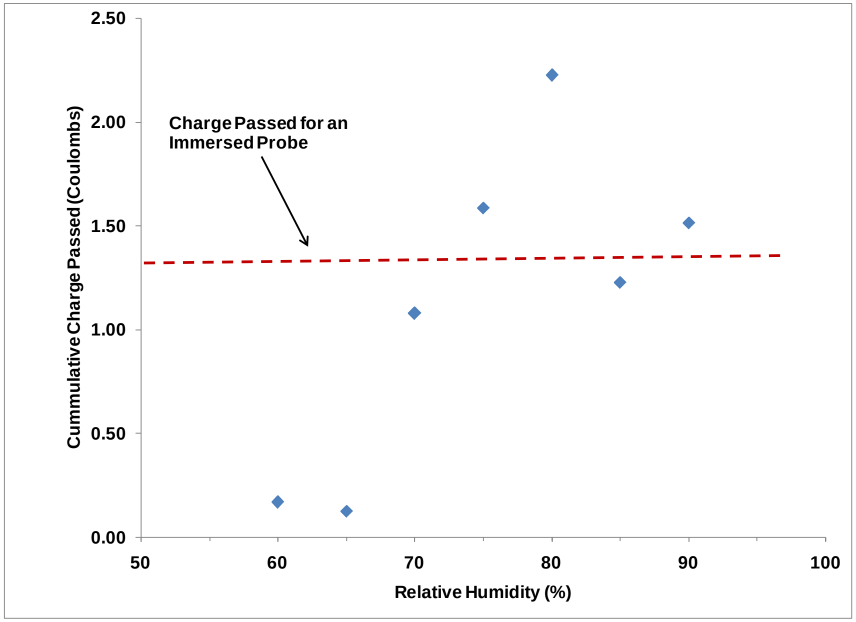
Multi-Electrode Measurements

- chamber assembled to control iso-humidity conditions
- Anodic and cathodic regions form on multi-electrode probe



Measurements at Iso-Humidity

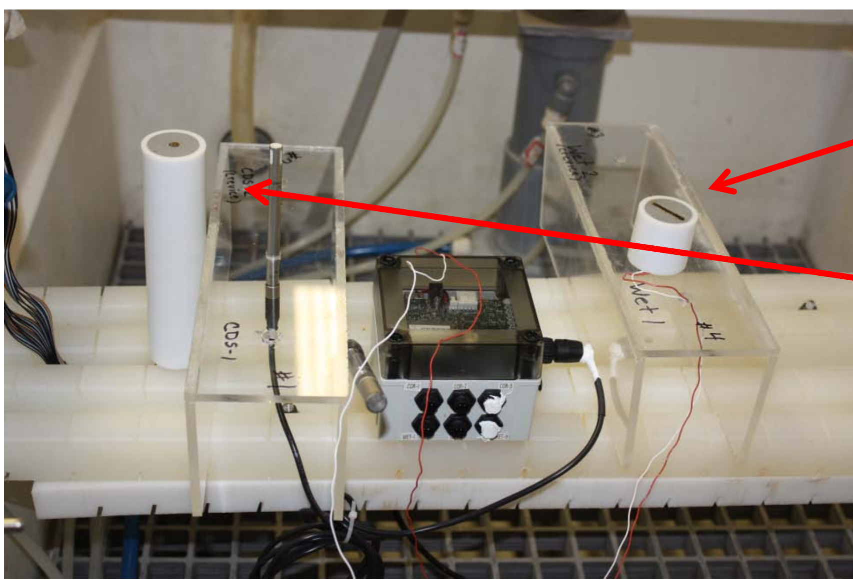




- Total anodic current vs. time shows different corrosion rates over time
  - < 70% is likely flash rust (short duration, electrolyte supports rust formation near 60% RH)
  - Anodic current peaks during wetting and drying
- Integration of current vs. time gives charge passed.
  - For NaCl covered surface and RH > 70%, , passed charge is similar to bulk liquid exposure

Measurements in Cyclic Humidity

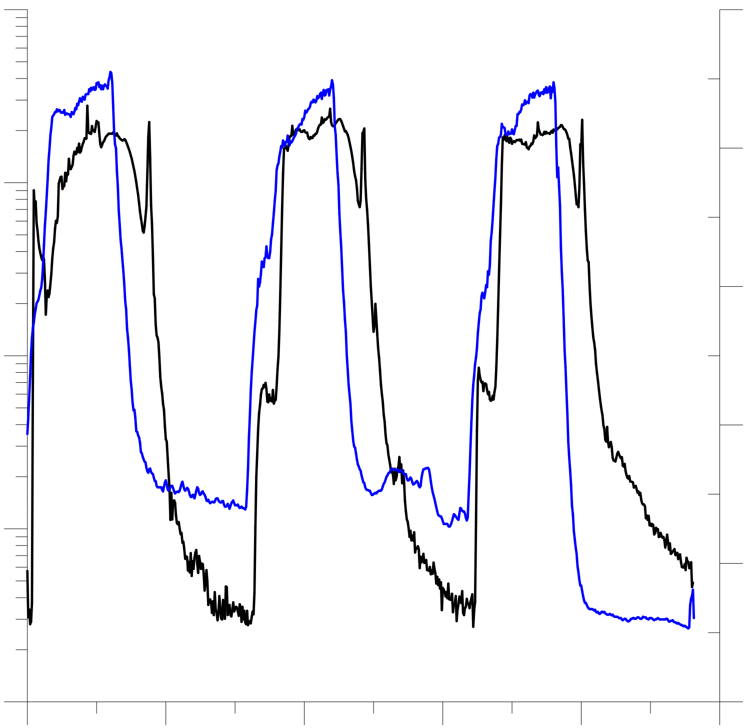
- How does wetting and drying affect corrosion processes?
- Tests performed in an AutoTechnology accelerated corrosion test chamber
- RH cycled between high and low values. Temp = 30^{o}C



Parallel plate wetness probe

MMA and RH probes

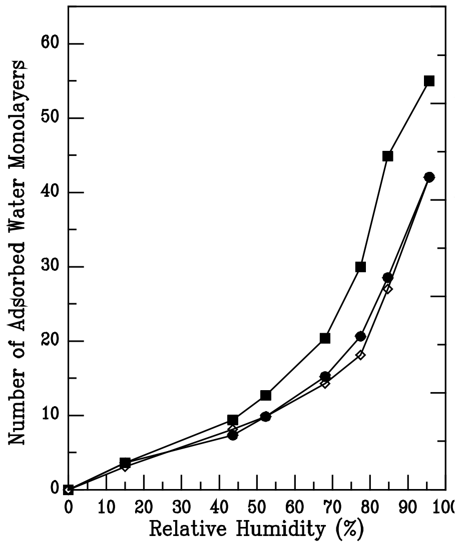
Measurements in Cyclic Humidity

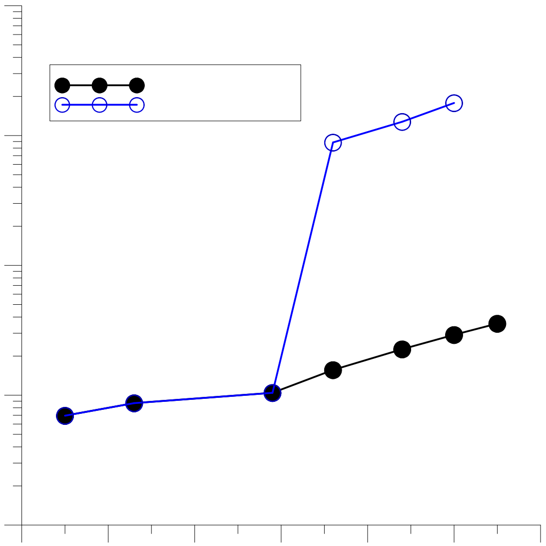


- Anodic current flows when RH is well below 40% and even as low as 15% during drying (efflorescence)
- Peaks in total anodic current are observed during wetting and drying
  - 60% - 65% = Thin film electrolyte behavior where initial high corrosion rate from oxygen availability followed by protective layer formation and decreasing corrosion rate
  - Above DRH = bulk electrolyte behavior + dissolved NaCl creating non-protective rust layer

Volume of Adsorbed Water

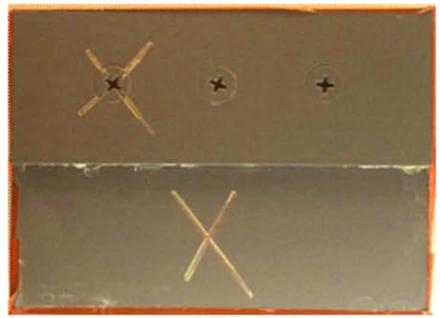
- Work by Dante and Kelly (1993) calculated adsorbed water onto Au
- Assuming Au and steel adsorption is similar and 30nl/cm^2/monolayer of water, can calculate volume of adsorbed moisture with salt
- OLI calculations used to calculate volume of water with NaCl deliquescence
- Corrosion of Steel can occur at 60% RH, would expect some protection since NaCl is not dissolved
- Above DRH, bulk water accumulation so would expect non-protective oxide

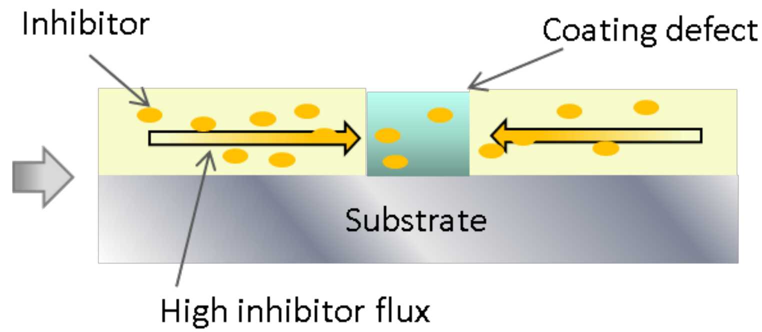




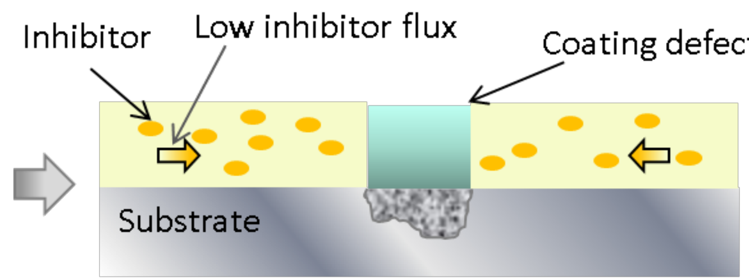
Hypothesis – Protection at a Scribe

Continuous salt fog





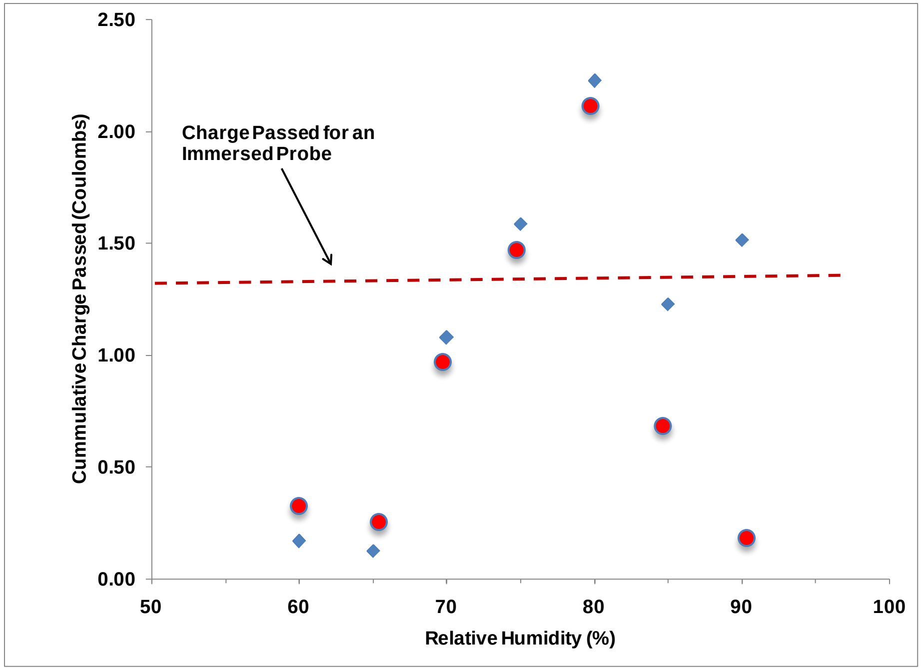
Dilute cyclic salt fog



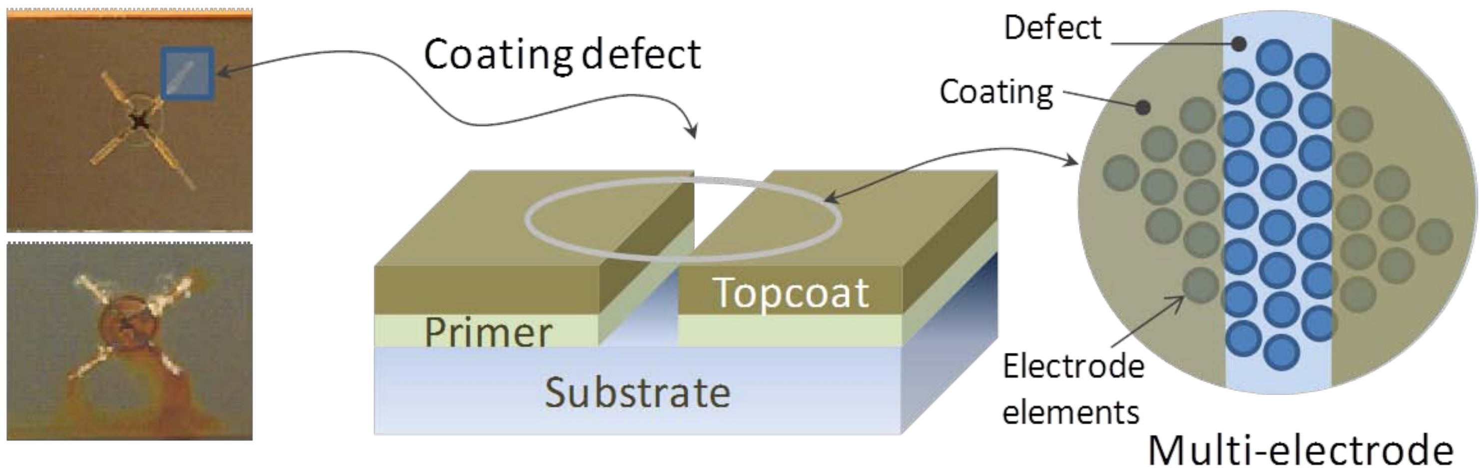
- Ability to protect substrate at a coating defect depends on connectivity between defect and mode of inhibition
- Moisture can promote inhibitor migration in the coating. For a given test method, wet and dry times will influence inhibitor mobility, and thus corrosion rate

Hypothesis – Protection at a Scribe

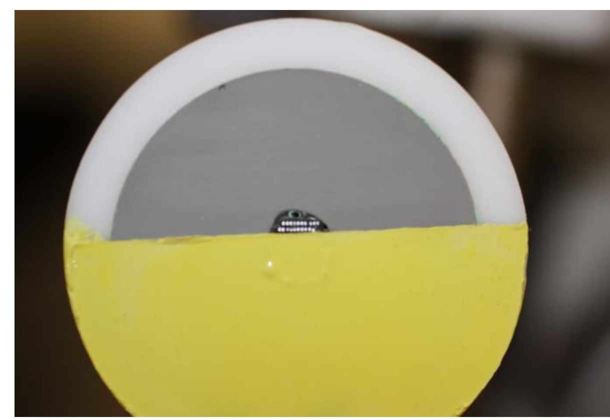
- For coated systems, what is the controlling process in corrosion failure at a scribe?
  - Corrosion rate of the substrate as a function of RH
  - Inhibitor mobility (or galvanic connectivity) (red dots are theoretical)



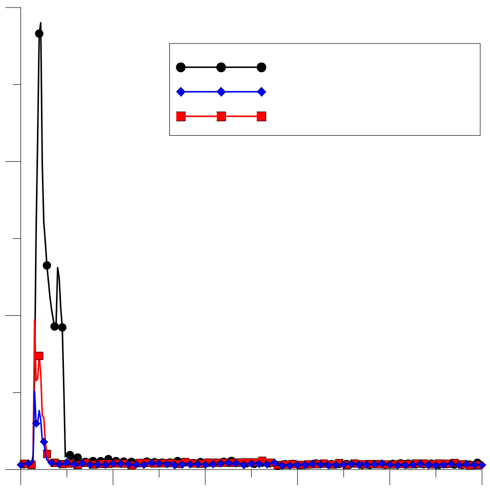
Simulation of Painted Surfaces

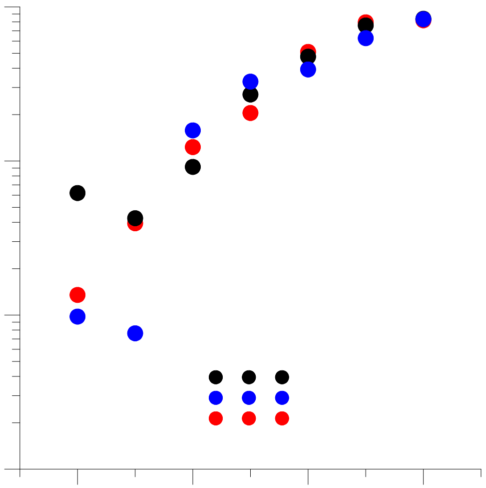


- Electrode surface painted leaving 20 electrodes (i.e. 2 rows) uncovered
- ½” o-ring placed over electrodes and salt deposited

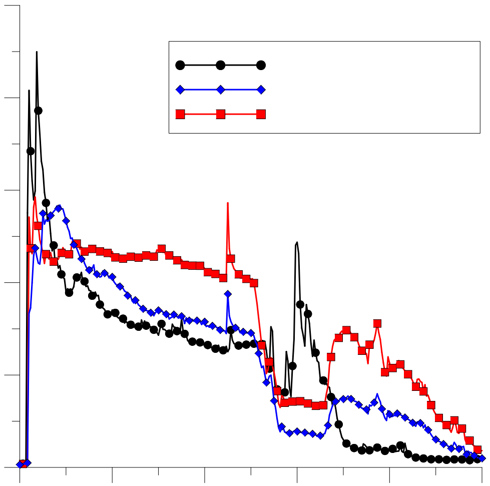


Effect of Inhibitor Leaching





- Inhibitors effect only below DRH
- Inhibitors suppresses the 60% RH peak for steel



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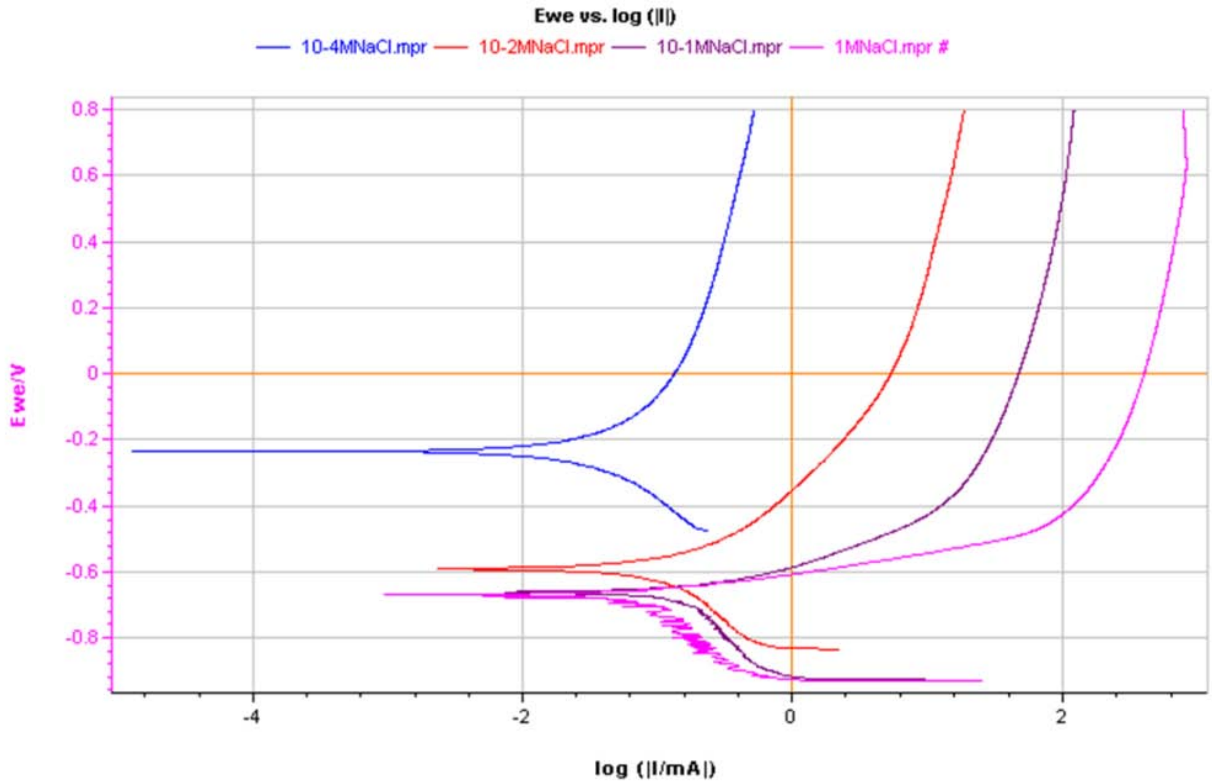

- Electrochemical potentiodynamic scans performed in NaCl + 0.001 M NaCl dichromate
- As NaCl decreases, cathodic current density increases
- Therefore, RH increases (NaCl decreases), total charge passed increases

Summary and Implications for Accelerated Testing

- Original hypothesis of chromate mobility decreasing with decreasing RH is not supported by the data
  - Component corrosion in cyclic environments controlled by galvanic interactions?
  - Need to determine what RH range results in decoupling of steel and aluminum
- Inhibitors protect against corrosion at 60% - 65% RH (flash rust) on steel
  - Short lived event that is likely inconsequential

Continuing Work

- Ongoing testing to define drying time as a function of
  - Time when RH > DRH
  - Drying time at differing RH values < DRH
- Testing using Aluminum electrodes